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GLASS FORMING ABILITY AND CRITICAL COOLING RATE FOR GLASS FORMATION IN BULK GLASS FORMING Ca-Mg-Zn ALLOYS

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ABSTRACT

A new Ca-Mg-Zn alloy having significantly improved glass forming ability (GFA) has been developed. The ternary $Ca_{65}Mg_{15}Zn_{20}$ bulk metallic glass (BMG) with diameter of at least 15 mm is successfully fabricated by conventional copper mold casting method in air atmosphere. The measured critical cooling rate (R_c) for glass formation in the cone-shaped copper mold is less than 20K/s. The R_c has been calculated from an integrated transformation curve constructed by combining continuous cooling transformation (CCT) and continuous heating transformation (CHT) curves. The calculated R_c is in good agreement with the measured value.

1. INTRODUCTION

Most of the bulk metallic glasses (BMGs) reported so far are based on the multi-component system to improve the atomic packing density in the liquid state. However, recently, simple ternary alloys such as Mg-Cu-(Y, Gd), Cu-(Zr, Hf)-Ti, Cu-Zr-Al, Ni-Nb-(Sn, Ti, Ta) and Ca-Mg-(Cu, Ni, Ag, Zn) have been reported to have high glass forming ability (GFA) enough to form BMGs.[1-4] These simple ternary alloys can be more suitable for commercial use, and provide a good opportunity for the study of glass-forming mechanisms. Although most of the BMGs necessitate the fabrication under controlled inert atmosphere in an evacuated closed chamber, some ternary BMGs such as in Mg-Cu-Gd system can be fabricated by conventional Cu-mold casting method in air atmosphere.[1] Such a rapid and simple production technique should greatly accelerated the potential wide-spread of BMGs in industrial products.

The Ca-rich Ca-Mg-Zn alloy system is expected to show high GFA due to: (1) large atomic size difference between the alloy elements (Ca: 1.97 Å; Mg: 1.60 Å; Zn: 1.38 Å); (2) large negative mixing enthalpy between the alloy elements (Ca-Mg: -20 kJ/mol; Ca-Zn: -72 kJ/mol; Mg-Zn: -13 kJ/mol); and (3) existence of a deep ternary eutectic reaction in the Ca-rich composition range. It has been reported that BMG samples with the diameter larger than 6 mm in a wide composition of Ca-rich Ca-Mg-Zn alloys are fabricated by conventional copper mold casting method in air atmosphere. The Ca-Mg-Zn alloy exhibits a significantly improved GFA when compared with Ca-Mg-M (M: Cu, Ni, Ag) alloys.[5]

The GFA can be expressed either by the critical cooling rate (R_c) for glass formation or the maximum-sectioned thickness (Z_c) of bulk metallic glass (BMG).[6] As the GFA increases, R_c decreases and Z_c increases. Therefore, proper estimation of R_c for glass formation of an alloy from thermal analysis data, which can be relatively easily obtained, will be helpful to develop a new alloy system having high GFA. Often the critical cooling rate, R_c^*, for glass formation has been calculated from the variation of solidification onset temperature, T_{xs} , with cooling rate, α, using following equation;[7,8]

$$\ln \alpha = \mathrm{R}_c' + \frac{d}{(T_L - T_m)^2} \qquad (1)$$

where T_L is the liquidus temperature, is a material factor. While the above relationship has been applied in many BMG systems, the estimation based upon

Eq. 1 showed a large discrepancy from experimentally measured data, as will be shown in this study.

During the solidification process, a liquid phase transforms into either a crystalline or an amorphous phase or a mixture of both. Even though the formation of crystalline phase is more thermodynamically favorable, the amorphous phase formation can take place if the cooling rate is fast enough to avoid the nucleation and growth of the crystalline phase. If a continuous cooling transformation (CCT) curve of liquid is successfully obtained, the critical cooling rate for glass formation can be calculated from the position of nose point.[9] Unfortunately, there is a difficulty in building a complete CCT curve across the whole temperature range between liquidus and glass transition temperature, especially below the nose temperature due to experimental limitations. It has been suggested that the identification of thermal stability of an amorphous phase during continuous heating transformation (CHT) curve can provide a kinetic boundary between glass and crystalline phase during heating.[10] Therefore, integrated transformation curves providing a global kinetic boundary between glass and crystalline phase in the entire temperature range between liquidus and glass transition temperature can be constructed by combining CCT and CHT curves, which are meaningful above and below a nose temperature, respectively.

In this study, the effect of alloy composition on the GFA of the Ca-rich Ca-Mg-Zn alloys was investigated in a wide composition range of 5 - 35 at % Zn and 5 - 25 at% Mg. Firstly, cone-shaped ingots and rod samples were prepared by conventional Cu-mold casting method and injection casting method in air atmosphere to evaluate the GFA. Secondly, a new method to estimate the critical cooling rate, R_c, for glass formation has been developed by building an integrated transformation curve, which is constructed by combining CCT and CHT curves. We have calculated the CCT and CHT curves from experimental measurements of cooling rate dependence of solidification onset temperature using classical nucleation kinetics and heating rate dependence of crystallization onset temperature by extension of Kissinger method, respectively. The critical cooling rate was estimated from the intersection point of the two curves, corresponding to the apparent nose point of the integrated transformation curve.

2. EXPERIMENTAL

High purity elements Ca (99.9%), Mg (99.9%) and Zn (99.9%) were alloyed in a graphite crucible in an Ar atmosphere using an induction furnace. After complete melting, the liquid alloy was poured into a copper mold in air atmosphere. The copper mold is cone-shaped with 45 mm in height, 15 mm in diameter at the top, and 6 mm in diameter at the bottom. From the ingots, injection cast samples with a diameter below 6 mm and rapidly solidified ribbon samples were fabricated for GFA evaluation and thermal analysis. Injection cast samples were prepared by re-melting the appropriate amount of the alloys in quartz tubes under a purified inert atmosphere followed by injecting through a nozzle into a Cu mold having cylindrical cavities of diameters varying from 1 to 5 mm. Rapidly solidified ribbon samples were prepared by re-melting the appropriate amount of the alloys in quartz tubes followed by ejecting with an over-pressure of 50 KPa through a nozzle onto a Cu wheel rotating with a surface velocity of 40 m/s. The resulting ribbons have a thickness of about 45 μm and a width of about 2 mm.

For the structural and thermal analysis, thin slices were cut from the as-cast cone-shaped ingots and injection-cast rod. The surfaces of the thin slices were examined by X-ray diffraction (XRD, Rigaku CN2301), with a monochromatic Cu K_α radiation. The thermal analysis of the as-melt-spun ribbons was carried out by differential scanning calorimetry (DSC, Perkin Elmer DSC7), using various heating rates between 0.083 and 1.334 K/s. Melting and solidification behavior of the specimens was monitored using differential thermal analyses experiments (DTA (Perkin-Elmer DTA7)). The liquidus temperature was assumed to be the end point of endothermic peak obtained during continuous heating with a heating rate of 0.667 K/s. The onset temperature of solidification (T_{sx}) during cooling was measured at various cooling rates between 0.03 and 0.5 K/s.

3. RESULTS AND DISCUSSION

3.1. Evaluation of GFA

Figure 1 shows composition ranges for BMG formation in Ca-rich Ca-Mg-Zn alloys investigated in the present study; and the symbols represent the

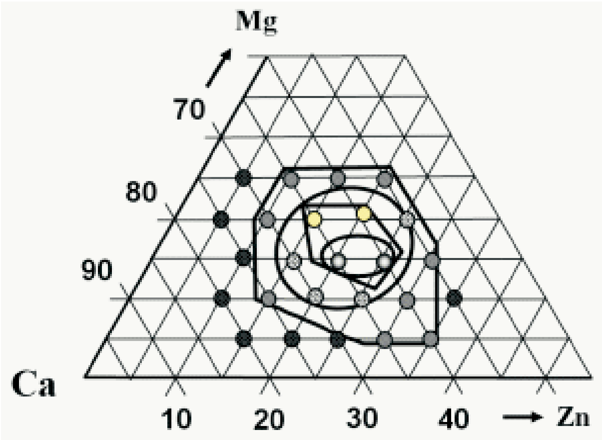

Fig. 1 : Map of composition ranges which can be form BMG samples in Ca-rich Ca-Mg-Zn alloys

composition ranges for D_{max} of < 1 mm, > 1mm, > 3mm, > 7 and > 10mm. The BMG formation shown in fig.1 was evaluated from the cone-shaped Cu-mold-cast ingots. However, the BMG formation for D_{max} < 6mm was evaluated from the injection-cast ingots due to the size limit of cone-shaped Cu-mold. The result in fig.1 showed that BMG samples with diameters larger than 1 mm can be fabricated in a wide composition range of 10 - 30 at% Zn and 5 - 25 at% Mg by conventional copper mold casting in air atmosphere. Among the alloys investigated, the $Ca_{65}Mg_{15}Zn_{20}$ and $Ca_{60}Mg_{15}Zn_{25}$ alloy exhibited excellent GFA enabling to form BMG sample with the diameter larger than 10 mm. In particular, the $Ca_{65}Mg_{15}Zn_{20}$ alloy exhibits the highest GFA enabling to form BMG sample with the 15 mm diameter.

3.2. Measurement and calculation of critical cooling rate

Figure 2 shows the cooling curves measured at the center of the three transverse cross sections, as indicated in Fig. 1. No evidence of heat release due to recalescence was observed, again confirming the formation of a single amorphous phase. The cooling rates measured at the center of the bottom, middle and top positions were ~149 K/s, ~93 K/s and ~20 K/s, respectively. The cooling rate for glass formation was obtained from $(T_l-T_g)/\Delta t$ where Δt is the range of time from T_l to T_g. Since the whole as-cast ingot has an amorphous structure, the critical cooling rate for glass formation in the $Ca_{65}Mg_{15}Zn_{20}$ alloy is less than ~20K/s. The measured critical cooling rates for glass formation shows a large variation depending on how easily heterogeneous nucleation occurs.[11] For Zr-Al-Ni-Cu-Pd BMG the critical cooling rate for the formation of glass is about 110K/s when measured during solidification in a wedge-type copper mold, which is similar to that

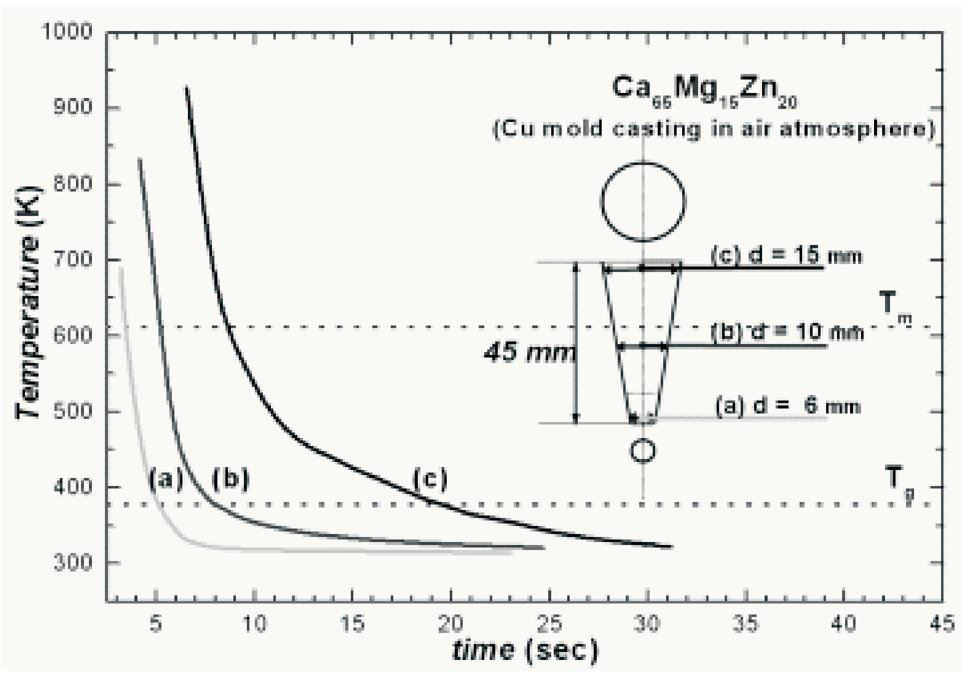

Fig. 2 : Cooling curves obtained from different positions: top, middle and bottom positions of the cone-shaped mold.

used in the present study, but decreases significantly down to the order of 10K/s when the number of heterogeneous nucleation sites are effectively reduced.

In order to complete the kinetic boundary of phase transformation from an undercooled liquid to a crystalline solid, the integrated transformation curve has been constructed by combining a continuous cooling transformation (CCT) curve and a continuous heating transformation (CHT) curve. Figure 3(a) shows a schematic illustration of the integrated transformation curve. The CCT curve gives a boundary for the onset of crystalline phase formation from liquid. However, the CCT curve is effective above a certain temperature. At lower temperature region, CHT curve is adopted to give a kinetic boundary between glass formation and crystalline phase formation. The CHT curve corresponds to the onset of crystallization of highly undercooled liquid. Then an integrated transformation curve is constructed by taking the CCT curve at high temperature region and CHT curve at lower temperature region. The CCT and CHT curves intersect at an intermediate temperature, which can be considered as an apparent nose temperature of the integrated transformation curve as shown in Fig. 3(a). If a cooling curve enters into the domain inside the integrated curve, nucleation of primary crystalline phase occurs and glass formation is not available. Therefore, the critical cooling rate for glass transition can be calculated form the intersection point as follow

$$R_c = \frac{T_L - T_{na}}{t_{na}} \qquad (2)$$

where and represent the temperature and time of the nose point, respectively.

Figure 3(b) shows the calculated integrated transformation curve for $Ca_{65}Mg_{15}Zn_{20}$ alloy together with thermal analysis data. Also two cooling curves obtained at the central axes of samples with different cross sectional diameters from a cone-shaped ingot are included. The cooling curve (2) measured at the center of cross section with a diameter of 10 mm passes away from the apparent nose point P1, indicating that the cooling rate is fast enough to form a glass. The cooling curve (1) measured at the center of cross section with a diameter of 15 mm passes near the apparent nose point P1 without crossing the integrated curve, indicating that the cooling rate is close to a critical cooling rate for glass transition. Also both cooling curves show no recalescence phenomenon, suggesting the suppression of crystalline phase formation. The calculated R_c for the $Ca_{65}Mg_{15}Zn_{20}$ alloy was 28 K/s, which is slightly higher than the mean cooling rate of 25 (+5) K/s from the cooling curve (1). Therefore, the glassy $Ca_{65}Mg_{15}Zn_{20}$ alloy could be formed by casting

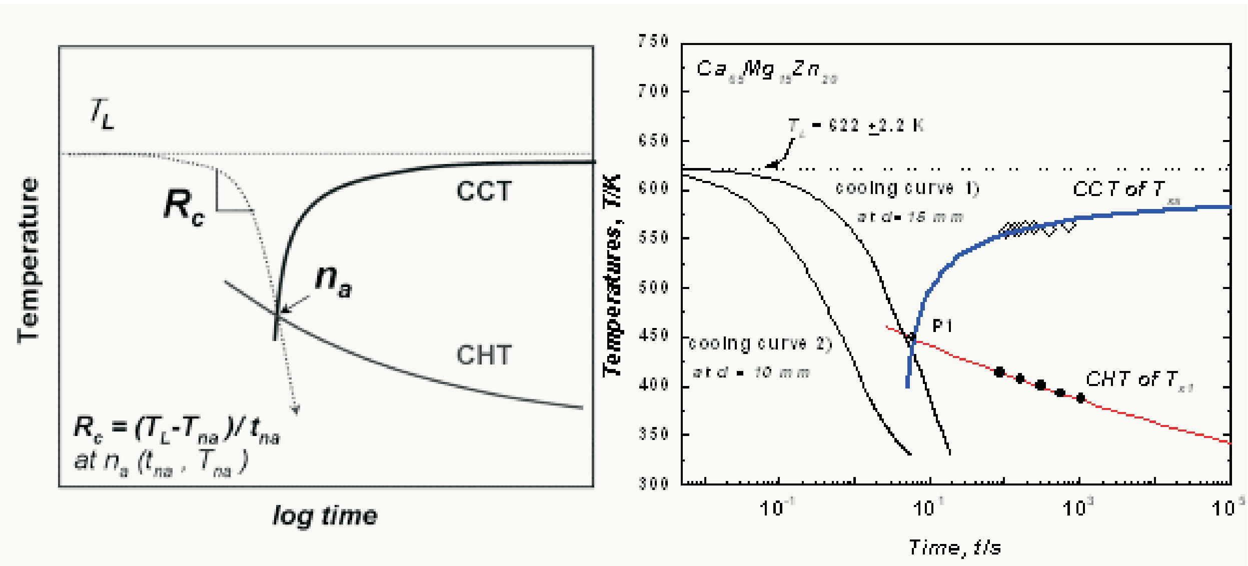

Fig. 3 : (a) Schematics of an apparent nose point, n_a, derived as a crossing point of a CCT curve and a CHT curve and a determination of a critical cooling rate for glass formation, R_c, obtained by using n_a. (b) Calculated CHT curve and calculated CCT curve for the amorphous $Ca_{65}Mg_{15}Zn_{20}$ alloy together with two cooling curves investigated at different diameters of the ingot.

process with a cooling rate over 28 K/s. This calculated critical cooling rate is in good agreement with the measured value of about 20 K/s.

The critical cooling rate calculated based on the newly suggested model in the present study, i.e. calculated from the intersection point , Fig 3(a), gives better agreement with the real experimental data than that calculated based on the previously suggested model, i.e. calculated using equation 1 (see introduction) [7,8]. Further verification of the suggested model is underway for other BMGs having different level of GFA.

4. SUMMARY

In a wide composition range of 10 - 30 at % Zn and 5 - 25 at % Mg BMG samples with the diameter larger than 1 mm are fabricated by conventional copper mold casting method under air atmosphere. Among the alloys investigated, the $Ca_{65}Mg_{15}Zn_{20}$ alloy exhibits the highest GFA enabling to form BMG sample with the diameter of at least 15 mm. From the cooling rate measurement in the cone-shaped copper mold, the critical cooling rate for glass formation is less than 20 K/s. The calculated R_c for the $Ca_{65}Mg_{15}Zn_{20}$ alloy was 28 K/s, which is slightly higher than the mean cooling rate of 25 (+5) K/s from the cooling curve 1). This calculated critical cooling rate is in good agreement with the measured value.

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REFERENCES

1. Men H, and Kim DH, *J of Mater Res* **18** (2003) 1502.
2. Inoue A, Zhang W, Zhang T and Kurosaka K, *Acta mater*. **49** (2001) 2645.
3. Choi-Yim H, Xu DH and Johnson WL, *Appl Phys Lett* **82** (2003) 1030.
4. Amiya K, and Inoue A, *Mater Trans* **43** (2002) 81.
5. Park E S, Kim W T, and Kim D H, *Mater Sci Forum* **475-479** (2005) 3415.
6. Uhlmann D R, *J Non-Cryst Solid* **7** (1972) 337
7. Barandiaran J M, and Colmenero J, *J Non-Cryst Solid* **46** (1981) 277.
8. Inoue A, Zhang T and Masumoto T, *J Non-Cryst Solid* **156-158** (1993) 473
9. Herlach D M, *Mat Sci and Eng*, **R12** (1994) 177
10. Louzguine D V, and Inoue A, *Appl Phy Lett* **81** (2002) 2561
11. Inoue A, Shinihara Y, Yokoyama Y and Masumoto T, *Mater Trans JIM* **36** (1995) 1276.